Studies on Dissociation Constants of Substituted Salicylic Acids in Ethanol-Water Mixtures by Conductometric Method

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Dissociation constants of 5-chloro- and 5-bromo-salicylic acids have been determined in water and aqueous ethanol (8 to 87·6%, w/w) by a modified version of the conductometric method suggested by Gelb. The results have been further checked by the method suggested by Fuoss and Kraus.

STUDIES on the dissociation constants of acids in different mixed and non-aqueous solvents have been made by different workers[1-14]. Most of the determinations were made by pH-metric method using appropriate corrections for mixed solvents or by potentiometric method where the emf of hydrogen electrode has been assumed to be zero in all the solvents and temperatures. The accuracy of pK values determined by spectrophotometric method ultimately depends on the accuracy of pH-measurements. The methods are likely to suffer[11,15-17] due to (i) liquid-junction potential of uncertain magnitude, (ii) loss of sensitivity of the glass electrodes, (iii) G_{H° is likely to change in different solvents.

A method which could avoid these uncertainties is essential for the determination of dissociation constants in mixed solvents. With this object in mind, we have determined the dissociation constants of 5-chloro- and 5-bromosalicylic acids in ethanol-water mixtures (8 to 87% by weight of ethanol) by a slight modification of the conductometric method suggested by Gelb[18]. The results have been further checked by the method suggested by Fuoss and Kraus[19,20].

Materials and Methods

CO$_2$-free doubly distilled water prepared from all glass distilling set was used for the preparation of the solutions. 5-chlorosalicylic acid and 5-bromosalicylic acid (BDH) were recrystallized from ethanol. The purity of the samples was checked by melting point determination. These acids and HClO$_4$ (GR, Merck) were estimated using standard NaOH (Merck) solution in the usual way. Succinic acid and potassium hydrogenphthalate utilized for the purpose were E. Merck's GR grade samples. The purification of ethanol and the weight percentages of the organic solvents in the solvent mixtures were determined in the same way as described earlier[21].

Conductance measurements were carried out using a Leeds and Northrup (model 4959) conductivity bridge with a sensitivity of $\pm 0·1\%$. A dip-type Philips conductance cell with cell constant, $\theta_1 = 0·815$ cm^{-1} was utilized. The measurements were carried out at $25° \pm 0·02°$.

In the titration method, known amounts of HClO$_4$ in appropriate solvents were added to the solutions of the organic acids at regular intervals and the mixtures were allowed sufficient time to attain equilibrium before measuring the conductance. The experiment was repeated with different concentrations of each acid and also in different percentages of organic solvents. The ionic strengths of the solutions were kept as low as practicable ($\approx 10^{-4}$ to $10^{-3}M$). The blank titrations were performed in the same way as described above, the experimental solutions being replaced by the same amount of the appropriate solvent. The conductances of the solvents were taken after applying appropriate corrections. Conductances of the acid solutions of different concentrations (1×10^{-4} to $5 \times 10^{-3}M$) were also measured.

Results

For a mixture of completely dissociated HClO$_4$ and partly dissociated organic acid HA (HA$\rightleftharpoons$H$^+$+A), the dissociation constant K can be written as shown in Eq. (1).

$$K = \frac{(\alpha C_{HA} + C_{HClO_4})}{(1-\alpha)} \times f_\pm^2 \qquad \ldots(1)$$

where C_{HA} = total concentration of HA, C_{HClO_4} = concentration of HClO$_4$ in the mixture, α = the degree of dissociation of HA in presence of HClO$_4$ and $f_\pm$ = mean activity coefficient.

The conductances of the mixtures (containing HA and HClO$_4$) and those of the blank solutions containing HClO$_4$ only) can be expressed by Eqs. 2 and 3.

$$\frac{1}{R} = \frac{1}{1000\,\theta_1}(C_{HClO_4}\Lambda'_{HClO_4} + \alpha C_{HA}\Lambda'_{HA}) \qquad \ldots(2)$$

and

$$\frac{1}{R*} = \frac{1}{1000\,\theta_1}C^*_{HClO_4}\Lambda'^*_{HClO_4} \qquad \ldots(3)$$

(*indicates the quantities in the blank solutions) where θ_1 = cell constant, $\Lambda' = \lambda_{cation} + \lambda_{anion}$ at the appropriate ionic strengths and $\Lambda = \alpha\Lambda'(\alpha = 1$ in the case of HClO$_4$). When $1/R = 1/R*$, we have

$$C^*_{HClO_4} \cdot \Lambda'^*_{HClO_4} = C_{HClO_4}\Lambda'_{HClO_4} + \alpha C_{HA} \cdot \Lambda'_{HA} \qquad \ldots(4)$$

Since C_{HClO_4} and $C^*_{HClO_4}$ do not differ considerably and the ionic strengths of the solutions are equal, we can write $\Lambda'_{HClO_4} = \Lambda'^*_{HClO_4}$. Due to the closeness of the mobility of ClO_4^- and anions, it is assumed that $\Lambda'_{HClO_4} = \Lambda'_{HA}$ in aqueous as well as in mixed solvents. This approximation leads to Eq. 5.

$$C_{HClO_4} + \alpha C_{HA} = C^*_{HClO_4} \qquad \ldots(5)$$

from which α can be calculated.

Modified equations[23] can be used to take into account the variations of Λ'_{HClO_4} and Λ'_{HA} due to variations of ionic strengths. But it is not necessary in the present case as the ionic strengths are kept sufficiently low and the change in ionic strength is too marginal to vitiate the assumption, $\Lambda^*_{HClO_4} = \Lambda'_{HClO_4}$ and $\Lambda'_{HClO_4} = \Lambda'_{HA}$, to a measurable accuracy. However, refinement of K values is possible taking

$$\alpha = (C^*_{HClO_4} - C_{HClO_4})/\beta\, C_{HA} \qquad \ldots(6)$$

where

$\Lambda'_{HClO_4} = \Lambda'^*_{HClO_4}$ and $\beta = \Lambda'_{HA}/\Lambda'_{HClO_4}$.

Instead of evaluating β values as suggested by Gelb, the equivalent conductances of HA and $HClO_4$ at infinite dilutions were determined and the ratio of Λ^o_{HA} and $\Lambda^o_{HClO_4}$ gave the value of β which can be regarded to be the ratio of Λ'_{HA} and Λ'_{HClO_4} in dilute solutions and at low ionic strengths.

The advantages of the method are that the accurate determination of cell constants are not necessary and the possibility of contamination of fairly strong acidic solutions with CO_2 diminishes.

Values of Λ^o_{HA} and K were also obtained from the plot of ΛC against $1/\Lambda$ for a number of dilute solutions (1×10^{-4} to $5 \times 10^{-3} M$) of HA using the Eq. 7.

$$\Lambda C = -K\Lambda^o + \Lambda^{o2}/\Lambda \qquad \ldots(7)$$

The intercept gives $(-K\Lambda^o)$ and the slope $K\Lambda^{o2}$. $\Lambda^o_{HClO_4}$ values at different concentrations of organic solvents were taken from our previous report[24].

The method, however, is an approximate one particularly for weak electrolytes and in solvents of low dielectric constants. The values of K and

Λ^o can be considerably improved by a method of computation used by Fuoss and Kraus utilizing Eq. 8.

$$\frac{F(Z)}{\Lambda} = \frac{1}{K\Lambda^{o2}} \cdot \frac{\Lambda C f_{\pm}^2}{F(Z)} + \frac{1}{\Lambda^o} \qquad \ldots(8)$$

The values of the Onsager constants, $\sigma = 82\cdot4$ $(\epsilon T)^{1/2}\eta$ and $\theta = \dfrac{8\cdot20 \times 105}{(\epsilon T)^{3/2}}$ used to calculate

$$Z\left(= \frac{(\theta \Lambda^o + \sigma)\sqrt{C\Lambda}}{\Lambda^{o3/2}} \right)$$

were calculated from the interpolated values of viscosities and relative permittivities of ethanol-water mixtures obtained from the data given by Shedlovsky et al.[25]. Previously determined Λ^o values in different percentages of mixed solvents, and θ and σ values were utilized to calculate Z and hence $F(Z)$.

The values of $\log f_{\pm}$ were calculated from Eq. 9

$$-\log f_{\pm} = A\sqrt{ac} \qquad \ldots(9)$$

using appropriate values of A in different mixed solvents.

However, the improvement in the values of K and Λ^o is very small in the present case, since the solutions under study are of low ionic strengths.

Discussion

The values of Λ^o and K of salicylic, 5-chlorosalicylic and 5-bromosalicylic acids are given in Table 1.

In spite of limited accuracy of the extrapolated Λ^o values, these appear (Table 1) to be in the expected order ($\lambda_{\text{salicylate}}$ ion = 35)[26]. Λ^o values decrease with increase in organic solvent in agreement with the observations of Shedlovsky and Kay[4].

The pK values for 5-chloro- and 5-bromosalicylic acids in water are $2\cdot65^{27}$ ($2\cdot63$)[28] and $2\cdot66^{27}$ ($2\cdot61$)[28] respectively. The present results agree well with these reported values. The results show that both the substituted acids are almost of equal strength as expected. The values in mixed solvents are lacking. However, considering the limitations and

TABLE 1 — DISSOCIATION CONSTANTS OF SUBSTITUTED SALICYLIC ACIDS

Wt % of EtOH	$(1/\epsilon) \times 10^2$	Λ^o		pK values of salicylic acid				pK values of 5-chlorosalicylic acid				pK values of 5-bromosalicylic acid			
		5-Chlorosalicylic acid	5-Bromosalicylic acid	a	a*	b	b*	a	a*	b	b*	a	a*	b	b*
0·0	1·27	395·0	394·1	3·04	3·05	3·09	3·04	2·65	2·66	2·71	2·66	2·61	2·62	2·75	2·66
8·0	1·35	345·5	352·0	3·08	3·12	3·16	3·12	2·71	2·73	2·76	2·72	2·69	2·75	2·78	2·74
16·4	1·42	283·0	283·6	3·19	3·24	3·31	3·27	2·85	2·88	2·88	2·84	2·75	2·80	2·88	2·85
25·3	1·53	235·2	235·0	3·38	3·43	3·47	3·42	2·98	3·03	3·10	3·05	2·87	2·93	3·07	3·03
34·4	1·71	180·3	177·0	3·47	3·54	3·59	3·56	3·07	3·14	3·20	3·18	3·04	3·08	3·26	3·20
44·0	1·90	154·1	157·1	3·71	3·76	3·82	3·77	3·33	3·36	3·42	3·40	3·26	3·31	3·47	3·41
54·1	2·14	133·5	130·8	3·97	4·03	4·04	4·01	3·45	3·54	3·62	3·60	3·43	3·50	3·60	3·57
64·7	2·44	112·5	110·5	4·13	4·23	4·30	4·27	3·67	3·74	3·84	3·78	3·66	3·75	3·82	3·79
76·0	2·87	90·7	84·3	4·48	4·57	4·63	4·60	4·11	4·15	4·23	4·20	4·09	4·13	4·19	4·17
87·6	3·37	67·2	64·8	4·82	4·93	5·06	4·99	4·41	4·45	4·49	4·47	4·45	4·48	4·52	4·50

(a) pK values from a plot of ΛC vs $1/\Lambda$. (a*) pK values after applying Fuoss-Kraus modifications. (b) pK values from the titration method. (b*) pK values after applying β correction.

the wide difference in the methods (Fuoss and Kraus and titration methods), the agreement is good.

The pK values increase sharply as dielectric constant decreases. This is expected due to increased solubility of molecular acids in organic solvents and the preferential hydration of H^+ ion by water molecules.

The pK values of salicylic acid in ethanol-water media have been reported by Grunwald and Berkowitz[1]. The agreement is fairly good only up to 52% (w/w) of ethanol beyond which there is a considerable deviation. It is a notable feature that the pK values obtained by conductometric method are a bit lower compared to those obtained by potentiometric methods as is apparent from pK values of acetic acid, obtained potentiometrically[29] and conductometrically[4] where agreement is good up to 40% (w/w) methanol.

The plots of pK values against $1/\epsilon$ ($\epsilon = $ relative permittivity) or mole fraction are linear, up to 65% (w/w) of ethanol beyond which deviations are observed. Marginal improvement is observed when the activity[30] of water is taken into consideration. The linearity is also good when pK (for the reaction $HA + A_0^- \rightleftharpoons HA_0 + A^-$) is plotted against $1/\epsilon$[31,32] as the method eliminates the proton accepting tendencies of the solvent systems.

The ΔpK_T values of these acids are almost the same within the limits of experimental error. This is quite relevant with acids of the same group. However, nothing can be visualized regarding the acid-base properties of the solvent systems. It is known that $\Delta pK_T = \Delta pK_{el} + \Delta pK_{nonel}$. The limitations of the calculations of ΔpK_{el} using Born equation[33] or modified Born equation[34,35] particularly with unsymmetrical electrolytes of unknown radii, are well known[11,16]. In view of difficulties in estimating the medium effects of ions and molecular species, discussion about the role of solvents on the dissociation constants and the ion-solvent interactions is difficult.

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